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CROSSLINKING AND FILLER REINFORCEMENT OF PERFLUOROALKYLENE TRIAZINE ELASTOMERS

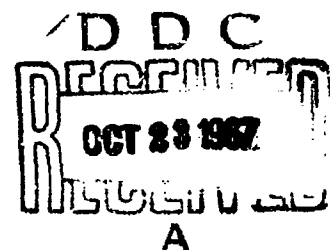
T. L. GRAHAM

TECHNICAL REPORT AFML-TR-66-402

AUGUST 1967

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CROSSLINKING AND FILLER REINFORCEMENT OF PERFLUOROALKYLENE TRIAZINE ELASTOMERS

T. L. GRAHAM

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FOREWORD

This report was prepared by the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, RTD, with Mr. T.L. Granam as project engineer. The work was initiated under Project 7340, "Nonmetallic and Composite Materials," Task 734005, "Elastomeric and Compliant Materials."

This report covers work accomplished during the period of April 1964 to September 1966.

The manuscript was released by the author September 1966 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.


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ABSTRACT

This exploratory compounding development program was conducted for the purpose of obtaining suitable modifiers for the crosslinking and reinforcing of triazine elastomers. The reinforcing effects of a variety of finely divided materials are compared. Data are presented showing the effect of concentration of the asbestos type filler (which yielded the most promising results) on the physical properties and thermal stabilities of a poly [perfluoropropylene (perfluoropropyl) triazine] gum and a blend comprised of equal parts of the gum and a poly [perfluoropropylene (perfluoropropyl) triazine] resin. Several organometallic and organic compounds were found to be effective crosslinking agents for poly [perfluorooctamethylene (perfluoropropyl) triazine] and n-perfluoropropylene cyanide modified poly [perfluorooctamethylene (perfluoropropyl) triazine] elastomers. The physical properties and thermal resistance of chemically vulcanized gums and asbestos reinforced vulcanizates based on the n-perfluoropropylene cyanide modified and unmodified poly [perfluorooctamethylene (perfluoropropyl) triazine] gums are discussed in detail.

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SECTION I

INTRODUCTION

Advanced Air Force weapon systems require elastomeric components such as O-ring seals, gasketing materials, filleting and faying surface sealants and wire insulation that can endure long periods at temperatures in excess of 400°F. Although, some commercial elastomers can withstand 400°F for an extended period, at higher temperatures the best of the available elastomers fail within a relatively short period because of embrittlement or reversion.

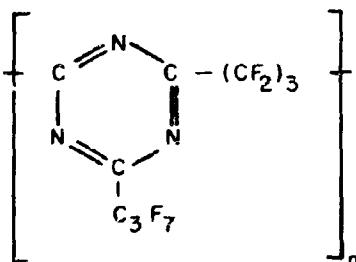
Polyperfluoroalkylene triazine is currently the prime experimental candidate elastomeric polymer under consideration for high temperature uses. Prior research has shown this type of polymer structure to have extraordinary thermal resistance at temperatures well in excess of 400°F. Samples of this polymer, after having been exposed at temperatures in the 600° to 800°F range, have retained their elastomeric characteristics. A major obstacle which has prevented this polymer from fulfilling some of the Air Force needs in the area of high temperature is the lack of a suitable means of obtaining crosslinked-reinforced products. In view of these facts internal research was initiated for the purpose of attaining the required modifiers for preparing crosslinked reinforced triazine products possessing good strength and thermal resistance at temperatures at least 100° above 400°F.

The triazine polymers used in this exploratory compounding research program were synthesized under Air Force Contracts AF33(616)-7963, AF33(657)-11252 and AF33(615)-1636 with the Hooker Chemical Corporation. Details concerning the synthesis of the polymer samples utilized in this research program are given in the reports referenced in the text of this report.

SECTION II

EXPLORATORY FILLER REINFORCEMENT INVESTIGATIONS

The initial polymeric triazine products, poly[perfluoropropylene (perfluoropropyl) triazine] having the idealized chemical structure shown below, were not particularly suitable for investigating crosslinking agents. The samples supplied were either hard-gelled resinous materials or stiff, partially gelled gums. Certain samples of the gum, however, could be processed and consequently were utilized for determining the relative effects of candidate reinforcing fillers.



POLY[PERFLUOROPROPYLENE (PERFLUOROPROPYL) TRIAZINE]

a. Candidate Filler Reinforcing Agents Screened

Several microfibrinous products, a couple of carbon blacks, several metal oxide powders, a perfluorinated poly-aromatic resinous product, and a few mineral fillers were screened in seeking suitable materials for the reinforcement of the triazine polymer. Because of the limited supply of a given sample of polymer, two separate samples of the poly[perfluoropropylene (perfluoropropyl) triazine] gum (Lots 1705-76* and 1705-87) (Reference 1) were involved in screening the selected candidate reinforcing agents. Since the presence of water was suspected of being undesirable, the fillers were heat treated to remove absorbed moisture. Compounds containing 15 phr of the selected fillers (in the case of Cab-O-Sil, 10 phr) were prepared for the investigation. All of the candidate reinforcing agents were incorporated and dispersed in the elastomer using a micro-mill.

The slabs required for determining tensile properties were formed by two different techniques. Slabs for the compounds in the first seven columns in Table I were obtained by banding the stock onto the micro-mill and cutting it off after forming a smooth band. This technique was used initially, since samples compression molded at 300°F, shrank and cracked upon cooling in the opened mold. It was later discovered, however, that this problem could be circumvented by compression molding at room temperature. Consequently, all subsequent samples involved in the exploratory filler screening investigations were compression molded at room temperature.

Since research (Reference 2) preceding these investigations had demonstrated that some degree of cure could be obtained by simply heating the polymer in air at an elevated temperature, these compounds were heat treated in air for 16 hours at 600°F.

*Lot 1705-76 is not referenced; Synthesis procedures for the preparation of Lot 1705-76 same as Lot 1705-67.

TABLE I
EFFECT OF CANDIDATE REINFORCING AGENTS ON THE PHYSICAL
PROPERTIES OF TRIAZINE GUM 1705-76

	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Triazine 1705-76	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon Wool 3B1	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Wilcarbo	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EPC Black	-	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Alon C	-	-	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pyrex A	-	-	-	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mineral Black #35	-	-	-	-	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-
Cib-C-Sil	-	-	-	-	-	-	-	-	10	-	-	-	-	-	-	-	-	-	-	-
Asbestos Superfine	-	-	-	-	-	-	-	-	-	15	-	-	-	-	-	-	-	-	-	-
Asbestine 3X	-	-	-	-	-	-	-	-	-	-	-	15	-	-	-	-	-	-	-	-
Texas V-2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	15	-	-	-	-
Asbestine Fine Texture	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Superglas 150C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	15	-	-	-
Heat Treated 16 Hours @ 600°F																				
Tensile Strength, psi	90	190	195	410	-	-	235	260	90	165	180	170	170	170	170	175	175	130		
Elongation, %	80	65	80	70	-	-	85	90	115	100	80	95	40	85	85	85	85	85		
Hardness, Shore A, Pts.	34	50	52	74	-	-	46	47	37	60	55	50	70	50	55	50	55	55		
Weight Loss, % (2)	-	-	-	-	-	-	-	-	18.8	20.6	19.6	18.9	19.3	18.8	19.3	18.8	18.8	19.9		
Aged in Air 72 Hours @ 700°F																				
Tensile Strength, psi	140	235	275	485	-	-	305	260	100	-(3)	425	295	275	375	250					
Elongation %	100	45	75	20	-	-	75	95	110	-	75	85	25	90	70					
Hardness, Shore A, Pts.	72	82	93	91	-	-	96	70	39	-	62	55	80	60	69					
Weight Loss, % (2)	-	-	-	-	-	-	-	-	22.2	39.9	18.2	14.8	18.2	15.1	35.3					

(1) The calcendered sample was spotted with cracks.

(2) Calculation based on weight of polymer.

(3) Extremely brittle.

Tensile data obtained on the thermally cured products before and after aging 72 hours at 700°F are summarized in Tables I and II. As these results show, all of the finely divided materials to varying degrees augmented the strength of these elastomeric triazine gums. The results, however, indicated the microfibrinous asbestos type extender to be the best choice. With these materials, marginal improvements in the thermal stability and significant increases in the tensile strength were obtained at nominal reductions in elongation. Although some of the other candidate extenders exhibited an equal or slightly greater reinforcing effect than the asbestos products, elongation and/or thermal stability were sacrificed.

b. Effects of Asbestine 3X Concentration on Poly[Perfluoropropylene (perfluoropropyl) Triazine] Gum

Additional samples of the poly[perfluoropropylene (perfluoropropyl) triazine] gum (Lot 1705-87) were extended with low to moderately high loadings (10 to 40 parts) of Asbestine 3X to further investigate the merits of the microfibrinous asbestos type material.

The data obtained on samples heat treated for 16 hours at 600°F and those obtained after 72 hours aging at 700°F are presented in Table III. Increases in tensile strength were realized with an increase in the concentration of this asbestos microfibrinous material. For the sake of preserving thermal stability and elongation, however, these results indicate that the concentration of asbestos should be limited to about 20 phr.

c. Effect of Asbestine 3X Concentration on Poly[Perfluoropropylene (perfluoropropyl) Triazine] Resin-Elastomer Blend

The Hooker Chemical Corporation obtained an elastomeric composite having a tensile strength of 1000 psi by blending a poly[perfluoropropylene (perfluoropropyl) triazine] resinous product with a poly[perfluoropropylene (perfluoropropyl) triazine] gum. As an extension of the Hooker work, research was conducted to investigate the merits of using asbestos filler in conjunction with a triazine resin for reinforcing triazine elastomers.

For this investigation compounds containing 0, 15, 30 and 45 phr of Asbestine 3X were prepared using a polymer blend comprised of equal parts of poly[perfluoropropylene (perfluoropropyl) triazine] gum (Lot 1705-87) and poly[perfluoropropylene (perfluoropropyl) triazine] resin (Lot 1705-69) (Reference 1).

A stability problem was encountered with the original compounds. When heated to cure at 600°F these samples sponged. Investigation of sponging revealed that it had been caused by volatile (easily sublimed) material released by the resinous triazine product. However, satisfactory thermally cured compounds were obtained using the fraction of this resinous polymer that was not volatile at 100°C under vacuum (2 to 3mm Hg).

The resin in conjunction with the asbestos filler yielded products of substantial strength (565 to 900 psi). Elongation, however, was sacrificed and the compounds proved to be extremely unstable (see Table IV).

TABLE II

EFFECT OF CANDIDATE REINFORCING AGENTS ON THE PHYSICAL PROPERTIES OF TRIAZINE GUM 1705-87

Triazine 1705-87	100	100	100	100	100	100
Perfluoropolyphenylene #2112	-	15	-	-	-	-
Amorphous Graphite #7	-	-	15	-	-	-
Crystalline Graphite #7	-	-	-	15	-	-
Tipersul	-	-	-	-	15	-
Baymal	-	-	-	-	-	15
<u>Heat Treated 16 Hours @ 600°F</u>						
Tensile Strength, psi	90	195	340	345	300	180
Elongation, %	130	95	70	80	50	70
Hardness, Shore A, Pts.	40	60	63	68	70	66
Weight Loss, % (1)	16.4	19.3	21.8	19.0	25.4	26.5
<u>Aged in Air 72 Hours @ 700°F</u>						
Tensile Strength, psi	110	95	425	550	- (2)	265
Elongation, %	120	130	50	45	-	30
Hardness, Shore A, Pts.	50	50	94	90	-	81
Weight Loss, % (1)	36.0	52.3	73.3	41.1	94.6	18.3

(1) Calculation based on weight of polymer.

(2) Extremely brittle.

TABLE III

EFFECT OF ASBESTINE 3X CONCENTRATION ON THE PHYSICAL PROPERTIES OF TRIAZINE GUM 1705-87

Triazine 1705-87	100	100	100	100	100	100
Asbestine 3X	-	10	15	20	30	40
<u>Heat Treated 16 Hours @ 600°F</u>						
Tensile Strength, psi	90	150	185	170	230	285
Elongation, %	130	125	130	125	95	70
Hardness, Shore A, Pts.	40	55	55	55	70	75
Weight Loss, % (1)	16.4	18.6	17.9	18.3	17.0	13.2
<u>Aged in Air 72 Hours @ 700°F</u>						
Tensile Strength, psi	110	185	345	310	415	390
Elongation, %	120	80	100	95	65	30
Hardness, Shore A, Pts.	50	65	70	70	85	90
Weight Loss, % (1)	36.0	41.3	31.7	34.2	43.9	47.7

(1) Calculation based on weight of polymer.

TABLE IV

EFFECT OF ASBESTINE 3X CONCENTRATION ON THE PHYSICAL
PROPERTIES OF A BLEND COMPRISED OF EQUAL PARTS OF
TRIAZINE RESIN 1705-69 AND TRIAZINE GUM 1705-87

Triazine Blend (1)	100	100	100	100
Asbestine 3X	-	15	30	45
<u>Heat Treated 16 Hours @ 600°F</u>				
Tensile Strength, psi	565	710	810	900
Elongation, %	65	50	30	30
Hardness, Shore A, Pts.	80	91	97	97
Weight Loss, % (2)	17.2	19.8	21.2	22.1
<u>Aged in Air 72 Hours @ 700°F</u>				
Tensile Strength, psi	360	165	- (3)	- (3)
Elongation, %	90	15	-	-
Hardness, Shore A, Pts.	80	88	-	-
Weight Loss, (2)	40.3	68.6	75.2	-

(1) 50/50: Triazine gel 1705-87/Triazine gel 1705/67.

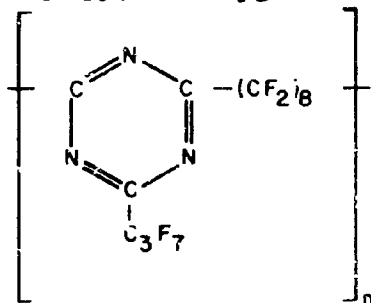
(2) Calculation based on weight of polymer.

(3) Extremely brittle.

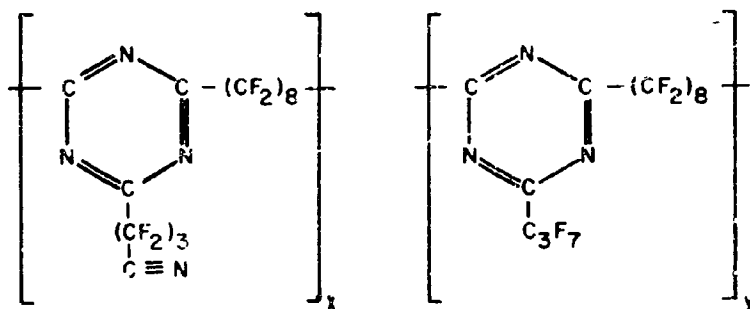
SECTION III

EXPLORATORY CHEMICAL CROSSLINKING INVESTIGATIONS

Samples of poly [perfluorooctamethylene (perfluoropropyl) triazine] and n-perfluoropropylene cyanide modified poly [perfluorooctamethylene (perfluoropropyl) triazine] gums (their idealized structures are shown below) were supplied at various intervals during this program and were used for crosslinking investigations. These later samples, although also partially gelled were more elastic and were more easily processed than the previous samples of gelled poly [perfluoropropylene (perfluoropropyl) triazine] gum.



POLY [PERFLUOROOCTAMETHYLENE (PERFLUOROPROPYL) TRIAZINE]



N-PERFLUOROPROPYLENE CYANIDE MODIFIED POLY [PERFLUOROOCTAMETHYLENE (PERFLUOROPROPYL) TRIAZINE]

A number of organometallic and non-metallic compounds and several mixtures comprised of metallic and non-metallic organic compounds were screened in seeking suitable curing agents for the above types of triazine gums. The selected candidate compounds were initially screened using poly [perfluorooctamethylene (perfluoropropyl) triazine] gum (Lot 1927-90-6).

a. Candidate Metallic Compounds

The metallic compounds evaluated are listed below:

Tetraphenyl Tin
Tetraphenyl Lead
Tetraphenyl Silicon
Tetraphenyl Germanium
Perfluorotetraphenyl Tin
Hexamethyl Borazole

Triphenyl Stibine
 B-Triphenyl Borazole
 Dibutyl Tin Mercaptopropionate
 Dibutyl Tin Bis(Lauryl Mercaptide)
 Dibutyl Tin Bis(Isooctyl Thioglycolate)
 Chromium Trifluoroacetate

Tetraphenyl Tin (which Hooker had shown in an earlier experiment to be an effective curing agent for the n-perfluoropropylene cyanide modified poly[perfluorooctamethylene (perfluoropropyl) triazine] gum was also effective for curing the above sample of poly[perfluorooctamethylene (perfluoropropyl) triazine] gum. The rate of reaction was very slow and was not observed to be significantly influenced by curing agent concentration. Increases in tensile strength were realized with increased concentration of tetraphenyl tin (Table V) but the tensile properties of the vulcanizates obtained using 2.5, 5 and 10 phr tetraphenyl tin were in general low. As shown in Figure 1 the vulcanizates proved to be less thermally stable than the uncured gum in the 580° to 630°F temperature range. In contrast to the 16 percent weight lost by the uncured gum in a 400-hour period, the tetraphenyl tin vulcanizates lost from 47 to 63 percent weight during this same period.

TABLE V
 TENSILE PROPERTIES OF TRIAZINE GUM 1927-90-6
 CURED WITH TETRAPHENYL TIN

Triazine 1927-90-6	100	100	100
Tetraphenyl Tin	2.5	5	10
<u>Initial Physical Properties</u>			
<u>Press Cured 20 Hours. @ 320°F</u>			
Tensile Strength, psi	245	285	325
Elongation, %	405	495	385
<u>Heated in Air 16 Hours @ 580° to 630°F</u>			
Tensile Strength, psi	180	125	115
Elongation, %	315	230	190
<u>Heated in Air an Additional 72 Hours @ 580° to 630°F</u>			
Tensile Strength, psi	125	110	115
Elongation, %	310	250	160

Tetraphenyl lead was the only other organometallic compound evaluated which yielded a structurally sound vulcanizate based on this particular sample of triazine gum. As the tensile data Table VI indicate, it was slightly less effective than tetraphenyl tin and yielded (see Figure 2) a relatively unstable vulcanizate.

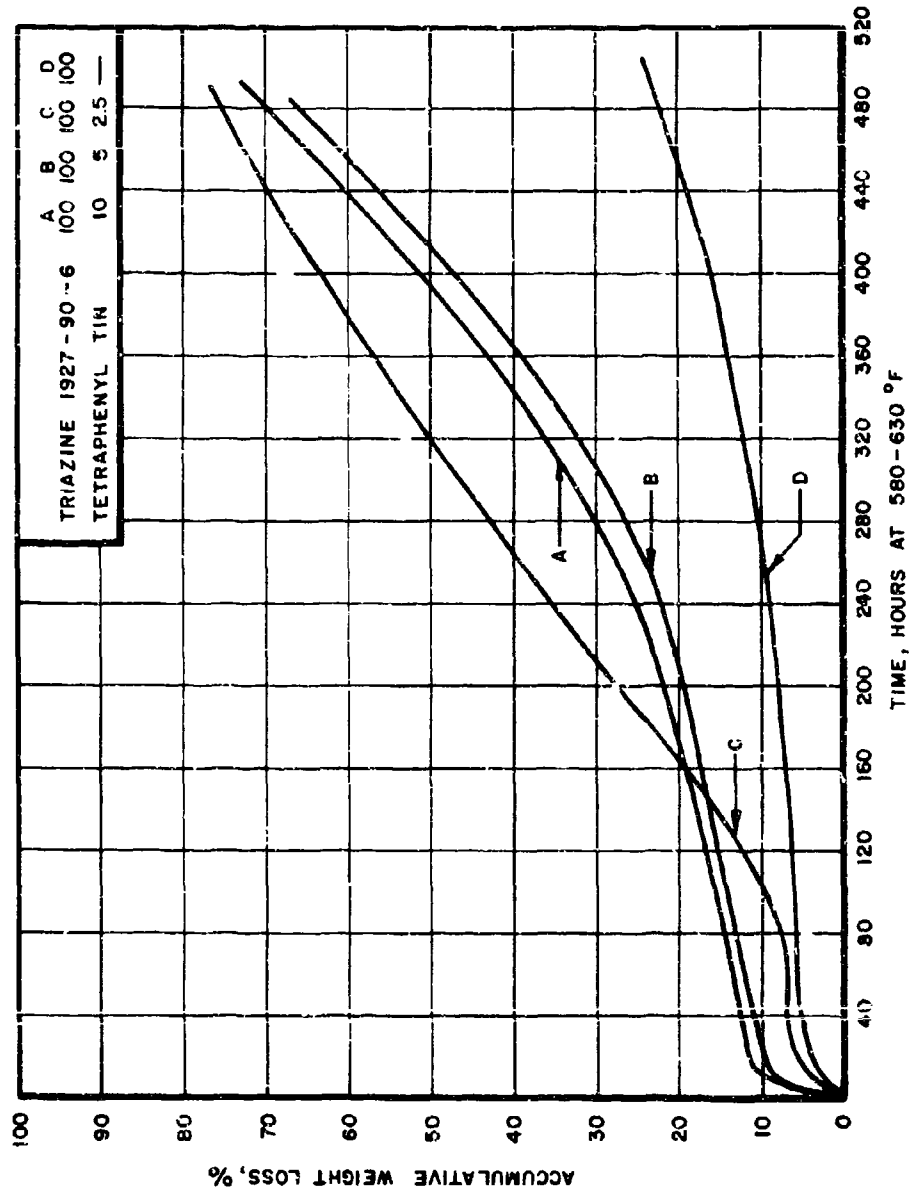


Figure 1. Thermal Stability of Triazine Gum 1927-90-6 Cured with Tetraphenyl Tin

TABLE VI

RELATIVE TENSILE PROPERTIES OF TRIAZINE GUM 1927-90-6
CURED WITH TETRAPHENYL TIN AND TETRAPHENYL LEAD

Triazine 1927-90-6	100	100
Tetraphenyl Tin	5	-
Tetraphenyl Lead	-	5
<u>Initial Physical Properties</u>		
<u>Press Cured 20 Hours @ 320°F</u>		
Tensile Strength, psi	285	235
Elongation, %	495	295
<u>Heated in Air 16 Hours @ 580° to 630°F</u>		
Tensile Strength, psi	125	160
Elongation, %	230	390
<u>Heated in Air an Additional 72 Hours</u>		
Tensile Strength, psi	110	135
Elongation, %	250	385

Adverse effects were obtained with perfluorotetraphenyl tin and hexamethyl borazole. These candidate curing agents appeared to decompose the gum. Triphenyl stibine proved to be inert. Partially cured porous products were obtained with the remaining candidate curing agents. The compounds prepared and the curing conditions used in the unsuccessful attempts to obtain crosslinked products are given in Table VII.

TABLE VII

TRIAZINE GUM 1927-90-6 COMPOUNDS CONTAINING OTHER
ORGANOMETALLIC CANDIDATE CURING AGENTS

	<u>Parts/100 Parts Triazine Elastomer</u>								
Perfluorotetraphenyl Tin	5								
Triphenyl stibine		5							
B-Triphenyl Borazole			5						
Hexamethyl Borazole				5					
Dibutyl Tin Mercaptopropionate					2.1				
Dibutyl Tin Bis (lauryl mercaptide)						2.1	2.1		
Dibutyl Tin Bis (isooctyl thiolglycolate)								2.1	
Chromium Trifluoroacetate									5
Press Cure Time @ 320°F, Hours.	20	20	20	20	18	0.5	16.5	17.5	1

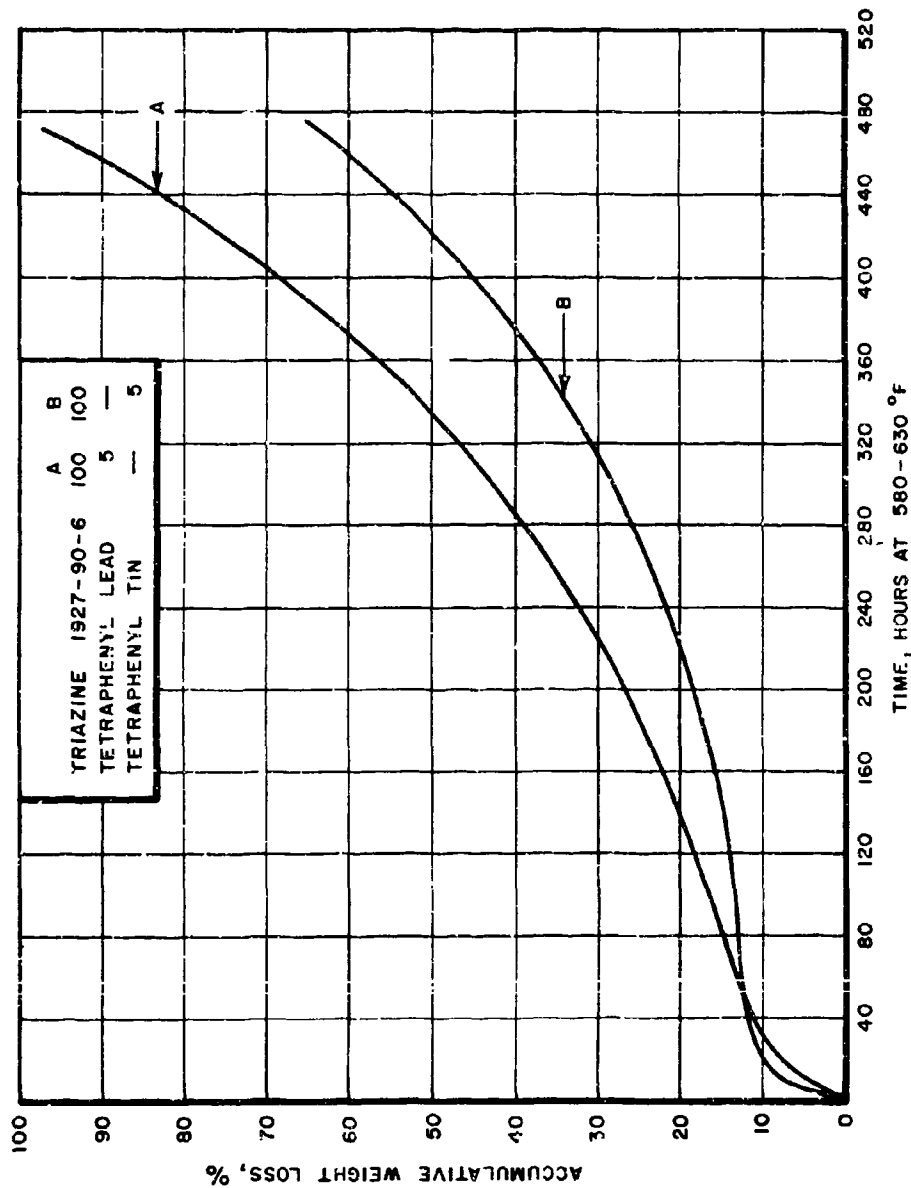


Figure 2. Relative Thermal Stability of Triazine Gum 1927-90-6 Cured with Tetraphenyl Tin and Tetraphenyl Lead

b. Candidate Non-metallic Compounds and Mixtures Comprised of Metallic and Non-metallic Compounds

The non-metallic organic compounds and compound mixtures screened are listed below:

1,3 Perfluorophenylene Diamine
 Perfluoroglutarimidine
 Perfluoroglutarimidine-Tetraphenyl Tin
 Perfluorosebaconitrile-Tetraphenyl Tin
 Perfluoroglutaronitrile-Hexabutyl Distannoxane
 Perfluorosebacamidine
 α, α -Diphenyl-m-Xylylidene Polymer
 Dicyclopentadiene Dioxide
 Triphenyl Phosphine

With the exception of perfluoroglutarimidine and the perfluoroglutarimidine-tetraphenyl tin mixture, the candidates listed above did not yield satisfactory vulcanizates. Perfluorophenylene diamine, triphenyl phosphine, dicyclopentadiene dioxide and α, α -diphenyl-m-xylylidene polymer appeared to degrade the triazine gum. Perfluoroglutaronitrile-hexabutyl distannoxane and perfluorosebaconitrile-tetraphenyl tin mixtures proved to be inactive. Undercured products spotted with voids were obtained with perfluorosebacamidine. The compositions of the compounds and the thermal treatments used in the unsuccessful attempts to obtain cured products are given in Table VII.

Rapid cures were obtained with perfluoroglutarimidine and a mixture comprised of equal parts of perfluoroglutarimidine and tetraphenyl tin. Tensile properties of these vulcanizates (Table IX) were similar to those of the tetraphenyl tin vulcanizates (shown in Table V). The perfluoroglutarimidine vulcanizate had a lower rate of weight loss than the gum cured with the mixture, (Figure 3) but became spotted with numerous tiny pinholes within the first several hours of exposure at 580° to 630°F.

In further attempting to obtain a thermally stable perfluoroglutarimidine vulcanizate a number of additional compounds were prepared wherein the concentration of curing agent as well as the cure time were varied over a broad range. A couple of vulcanizates were also prepared using purified (freshly sublimed) perfluoroglutarimidine. As an additional precaution the gum used in the preparation of one of these samples was also preheated at 600°F for approximately 472 hours to remove volatiles.

These modifications did not produce the expected improvement. Within 48 hours or less at 600°F these additional perfluoroglutarimidine vulcanizates (Table X) lost their structural integrity.

TABLE VIII
 TRIAZINE GUM 1927-90-6 COMPOUNDS CONTAINING NON-METALLIC AND MIXTURES
 OF METALLIC AND NON-METALLIC COMPOUNDS AS CANDIDATE CURING AGENTS

	Parts/100 Parts Triazine Elastomer							
	5	4 drops 5	several drops several drops	1	5	10	5	5
1,3 Perfluorophenylene Diamine								
Perfluorosebacnitrile								
Tetraphenyl Tin								
Perfluoroglutaronitrile								
Hexabutyl Distannoxane								
Perfluorosebacamidene								
α, α Diphenyl-m-xylylidene Polymer								
Dicyclopentadiene Dioxide								
Triphenyl Phosphine								
Press-Cure Time @ 320° F, hours	20	1	1	1	1 1/4	4	1 1/2	64 1/2
Press-Cure Time @ 600° F, hours							3 1/2	64 1/2

TABLE IX

TENSILE PROPERTIES OF TRIAZINE GUM 1927-90-6 CURED WITH
PERFLUOROGLUTARIMIDINE AND A MIXTURE OF PERFLUORO-
GLUTARIMIDINE AND TETRAPHENYL TIN

Triazine 1927-90-6	100	100
Perfluoroglutarimidine	5	5
Tetraphenyl Tin	5	-
Initial Physical Properties		
Press Cure Time @ 320° F, Min.	20	4
Tensile Strength, psi	220	230
Elongation, %	480	590
Heated in Air 16 Hours @ (580° To 630° F)		
Tensile Strength, psi	265	- (1)
Elongation, %	320	-
Heated in Air an Additional 72 Hours @ (580° To 630° F)		
Tensile Strength, psi	135	-
Elongation, %	245	-

(1) Weight Loss data only

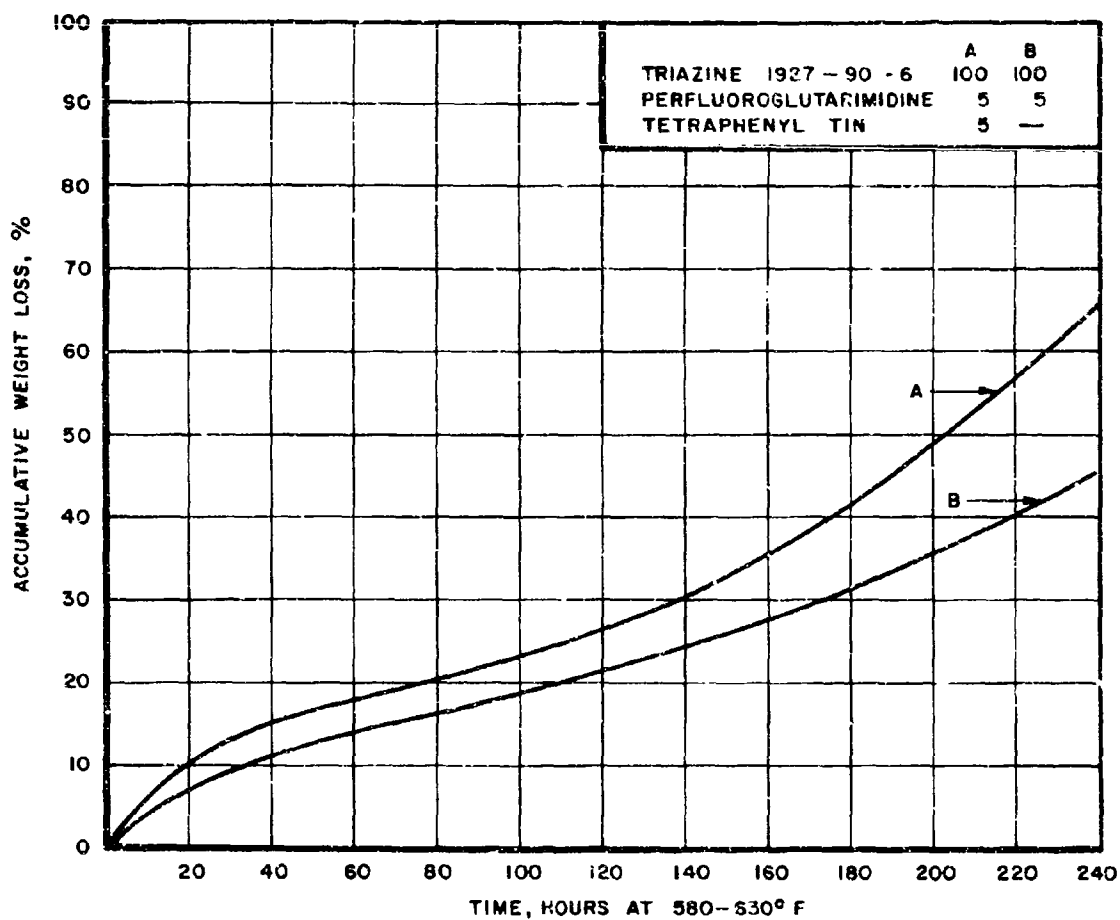


Figure 3. Relative Thermal Stability of Triazine Gum 1927-90-6 Cured with Perfluoroglutarimidine and a Mixture of Perfluoroglutarimidine and Tetraphenyl Tin

TABLE X
ADDITIONAL TRIAZINE GUM 1927-90-6 COMPOUNDS CURED WITH PERFLUOROGUTARIMIDINE

Perfluoroglutarimidine Perfluoroglutarimidine (Freshly Sublimed) Press-Cure Time at 320° F, Hours	Parts/100 Parts Triazine Elastomer									
	5	10	10	15	1	2.5	5	10	20	10 (1)
	1	1	20	1/3	3	3	3	3	3	1

(1) Triazine gum preheat treated @ 600° F for 472 hours to remove volatile material.

SECTION IV

CURING CHARACTERISTICS OF ADDITIONAL EXPERIMENTAL LOTS OF POLY
[PERFLUOROOCTAMETHYLENE (PERFLUOROPROPYL) TRIAZINE] GUMS.

Several compounds were prepared using other samples (Lots 2215-71-1 and 2227-48-1) of the poly[perfluorooctamethylene (perfluoropropyl) triazine] gum supplied later in the program in further exploiting tetraphenyl tin and perfluoroglutarimidine as curing agents. The compositions prepared and the curing cycles used are summarized in Table XI.

The results were unsatisfactory. The tetraphenyl tin compounds based on these later experimental gums yielded undercured products containing voids. Although satisfactory vulcanizates were obtained using perfluoroglutarimidine, these vulcanizates became porous within approximately 16 hours at 600°F.

TABLE XI

ADDITIONAL EXPERIMENTAL POLY [PERFLUOROOCTAMETHYLENE (PER-
FLUOROPROPYL) TRIAZINE] GUM-CURING AGENT COMPOUNDS EVALUATED

Triazine 2215-71-1	100	-	-	100	-
Triazine 2227-48-1	-	100	100	-	100
Tetraphenyl Tin	5	5	10	-	-
Perfluoroglutarimidine	-	-	-	10	10
Press-Cure Time @ 320° F, Hours	20	20	20	2	2

SECTION V

CURING CHARACTERISTICS OF EXPERIMENTAL TRIAZINE GUMS
CONTAINING n-PERFLUOROPROPYLENE CYANIDE PENDANT GROUPS

A couple of samples of poly[perfluorooctamethylene (perfluoropropyl) triazine] gum containing theoretically 20 mole % n-perfluoropropylene cyanide pendant groups were utilized when further attempting to obtain a thermally stable cured product. One sample of this particular species of the triazine gum (Lot 2227-49 1) (Reference 3) proved to be very reactive towards many of the compounds previously screened. In addition to obtaining cured samples using tetraphenyl tin and perfluoroglutarimidine, adequate states of cure were obtained with tetraphenyl silicon, perfluorosebacamidine and mixtures of the latter two compounds. A structurally sound vulcanizate was also obtained with tributylantimony oxide, one of the two new candidate curing agents evaluated. Perfluorosebacic acid, the other new candidate curing agent, appeared to degrade this polymer. Although perfluorosebacamidine proved to be an effective compound for curing the other sample of modified triazine gum (Lot 15B), (Reference 3) satisfactory vulcanizates were not obtained using tetraphenyl tin. The compositions of the compounds prepared with these elastomer samples are given in Table XII.

The cured products proved to be inadequately stable at 600°F. The perfluoroglutarimidine and the perfluorosebacamidine vulcanizates became spotted with pinholes within 16 hours. Vulcanizates obtained using tributyl antimony oxide, tetraphenyl silicon, tetraphenyl tin, perfluorosebacamidine and mixtures of the latter two compounds lost weight rapidly at 600°F (Figure 4).

TABLE XII

n-PERFLUOROPROPYLENE CYANIDE MODIFIED POLY [PERFLUOROOCTAMETHYLENE (PERFLUOROPROPYL) TRIAZINE] GUM-CURING AGENT COMPOUNDS EVALUATED

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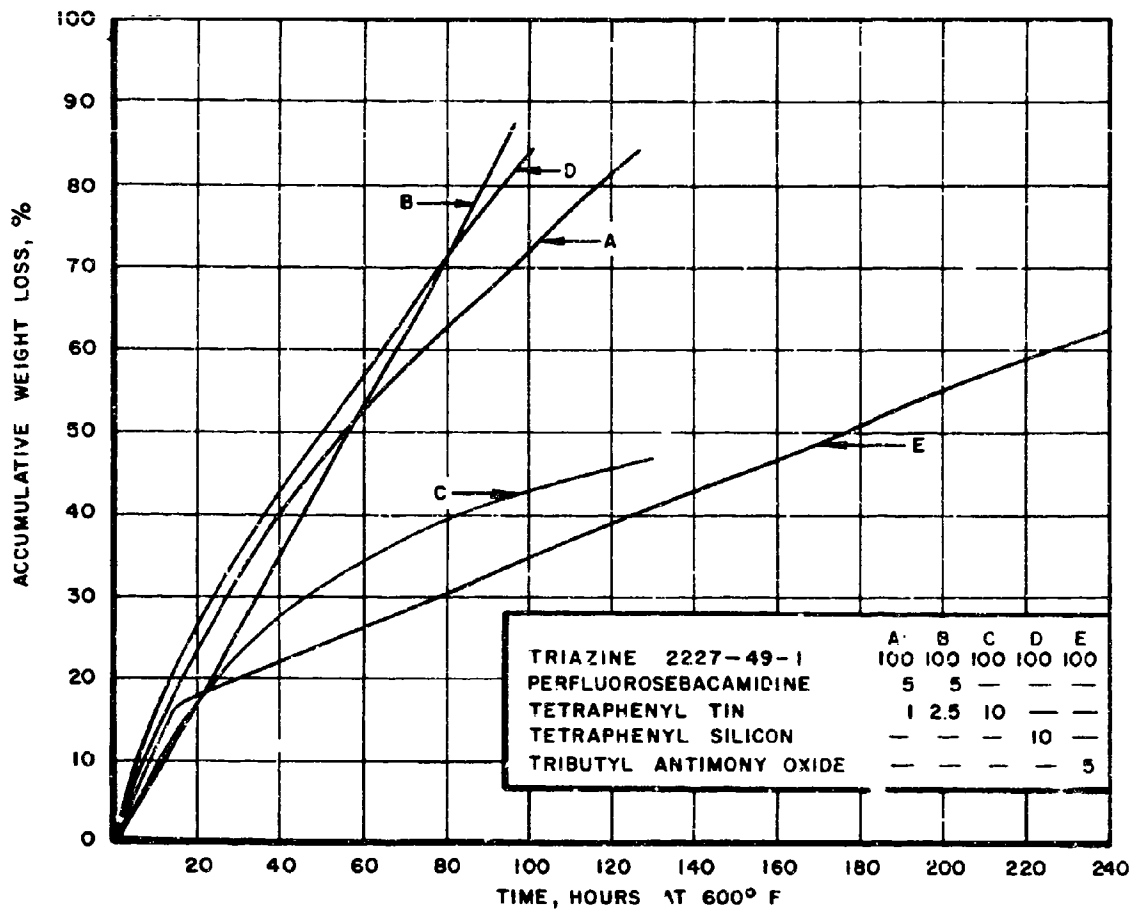


Figure 4. Relative Thermal Stability of Several Chemically Cured Vulcanizates Based on n-Perfluoropropylene Cyanide Modified Triazine Gum 2227-49-1

SECTION VI

ASBESTOS REINFORCED CHEMICALLY CROSSLINKED
TRIAZINE VULCANIZATES

Several gum vulcanizates and asbestos extended chemically cured compounds based on the n-perfluoropropylene cyanide modified and unmodified species of the poly[perfluorooctamethylene (perfluoropropyl) triazine] gums were prepared to determine the overall merits of asbestos as a reinforcing agent and to obtain 500°F aging data.

The compositions of the vulcanizates based on the poly[perfluorooctamethylene (perfluoropropyl) triazine] gums and the tensile data obtained are presented in Table XIII. Comparable data and the compositions of vulcanizates based on the n-perfluoropropylene cyanide modified poly[perfluorooctamethylene (perfluoropropyl) triazine] gums are shown in Table XIV.

As is apparent from the data, original tensile strengths of the asbestos reinforced vulcanizates were 200 to 300 psi greater than the unreinforced gum vulcanizates. The tensile strength of all the vulcanizates increased following various periods of exposure at 500°F. These gains in tensile strength were most likely due to thermally induced polymer rearrangements and were accompanied by losses in weight.

Contrary to previous results, the asbestos filler for the most part had an adverse effect on thermal stability (Figures 5 and 6). The rates of weight loss were generally greater for the asbestos reinforced vulcanizates than for the unreinforced cured gums as well as the uncured gums. As the plotted weight loss data show, vulcanizates based on the asbestos reinforced poly[perfluorooctamethylene (perfluoropropyl) triazine] gum were more thermally resistant than the asbestos reinforced vulcanizates based on the n-perfluoropropylene cyanide modified poly[perfluorooctamethylene (perfluoropropyl) triazine] gum. Although the rates of weight loss decreased with time, the former vulcanizates lost from 21 to 26 percent of their weight within a period of 500 hours at 500°F.

TABLE XIII

TENSILE PROPERTIES OF ASBESTINE 3X EXTENDED POLY
[PERFLUOROOCTAMETHYLENE (PERFLUOROPROPYL)
TRIAZINE] VULCANIZATES

Triazine 2215-71-1	100	100	-	-	-
Triazine 2227-48-1	-	-	100	100	-
Triazine 1927-90-6	-	-	-	-	100
Perfluoroglutarimidine	10	10	10	10	-
Tetraphenyl Tin	-	-	-	-	10
Asbestine 3X	-	20	-	20	20
Original					
Tensile Strength, psi	240	445	230	425	730
Elongation, %	210	175	105	105	600
After 16 hours @ 500° F					
Tensile Strength, psi	365	730	360	750	1005
Elongation, %	165	130	200	145	225
After 72 hours @ 500° F					
Tensile Strength, psi	440	770	335	820	540
Elongation, %	195	100	185	140	295
After 10 days @ 500° F					
Tensile Strength, psi	490	885	355	925	-
Elongation, %	115	115	200	115	-
After 20 days @ 500° F					
Tensile Strength, psi	-	-	-	-	505
Elongation, %	-	-	-	-	230
After 24 days @ 500° F					
Tensile Strength, psi	285	340	225	345	-
Elongation, %	175	130	165	130	-

TABLE XIV

TENSILE PROPERTIES OF ASBESTINE 3X EXTENDED VULCANIZATES
 BASED ON POLY[PERFLUOROOCTAMETHYLENE (PERFLUOROPROPYL)
 TRIAZINE] GUMS CONTAINING n-PERFLUOROPROPYLENE CYANIDE
 PENDANT GROUPS

Triazine 15B	100	100	--	-
Triazine 2227-49-1	-	-	100	100
Perfluorosebacamide	10	10	10	10
Asbestine 3X	-	20	-	20
Original				
Tensile Strength, psi	375	675	775	1035
Elongation, %	135	125	1	105
After 16 hours @ 500° F				
Tensile Strength, psi	510	630	710	1375
Elongation, %	150	80	130	115
After 72 hours @ 500° F				
Tensile Strength, psi	445	365	335	1275
Elongation, %	125	80	70	75
After 10 days @ 500° F				
Tensile Strength, psi	335	520	- (1)	1400
Elongation, %	135	95	-	65

(1) This vulcanizate after 10 days at 500° F contained numerous bubbles.

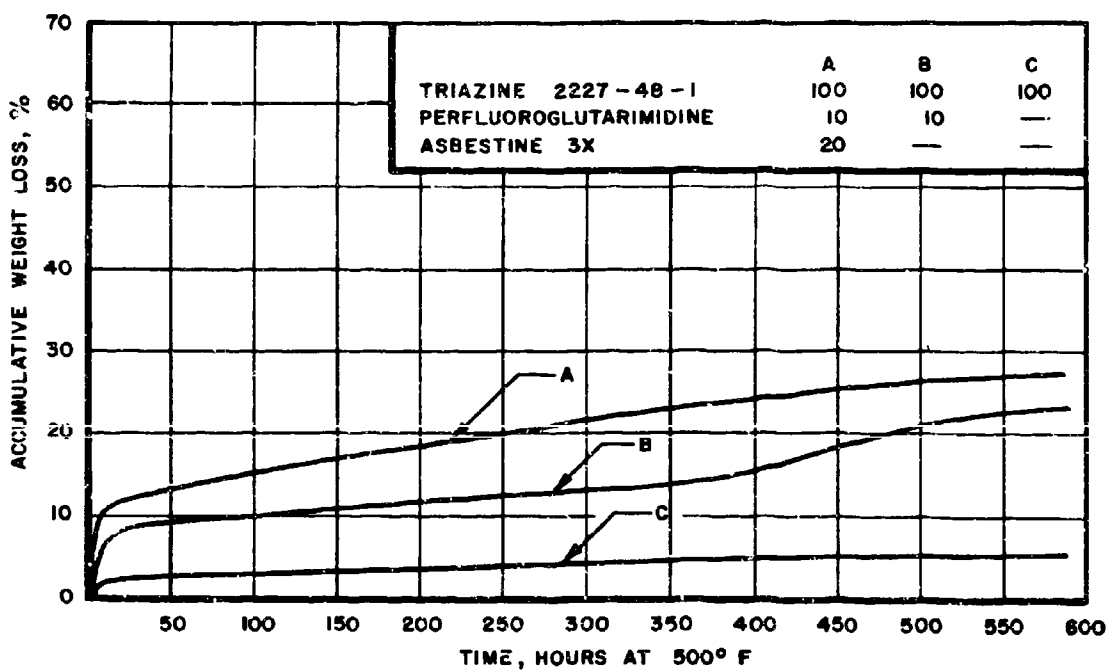
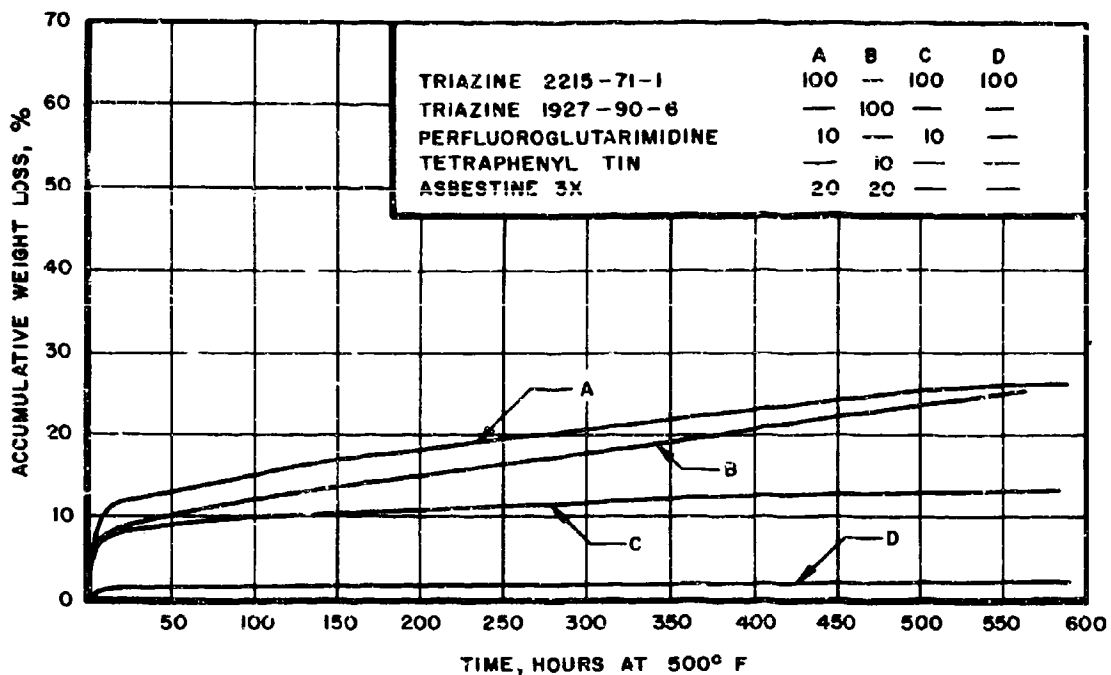


Figure 5. Effect of Asbestine 3X on the Thermal Stability of Vulcanizates Based on Poly [perfluorooctamethylene (perfluoropropyl) Triazine] Gums

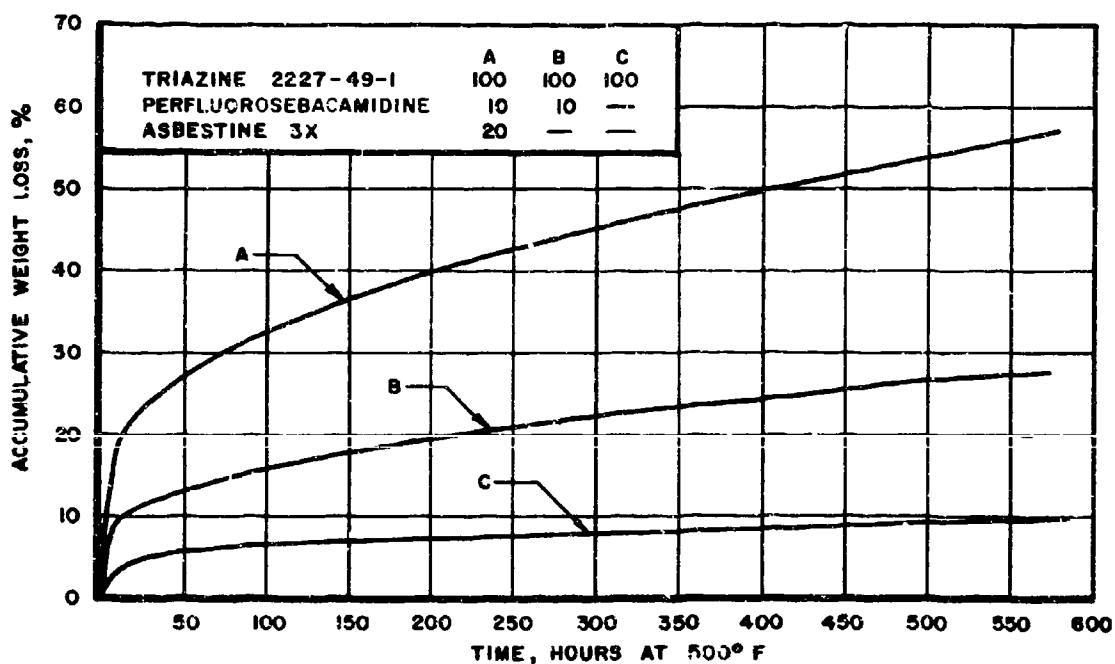
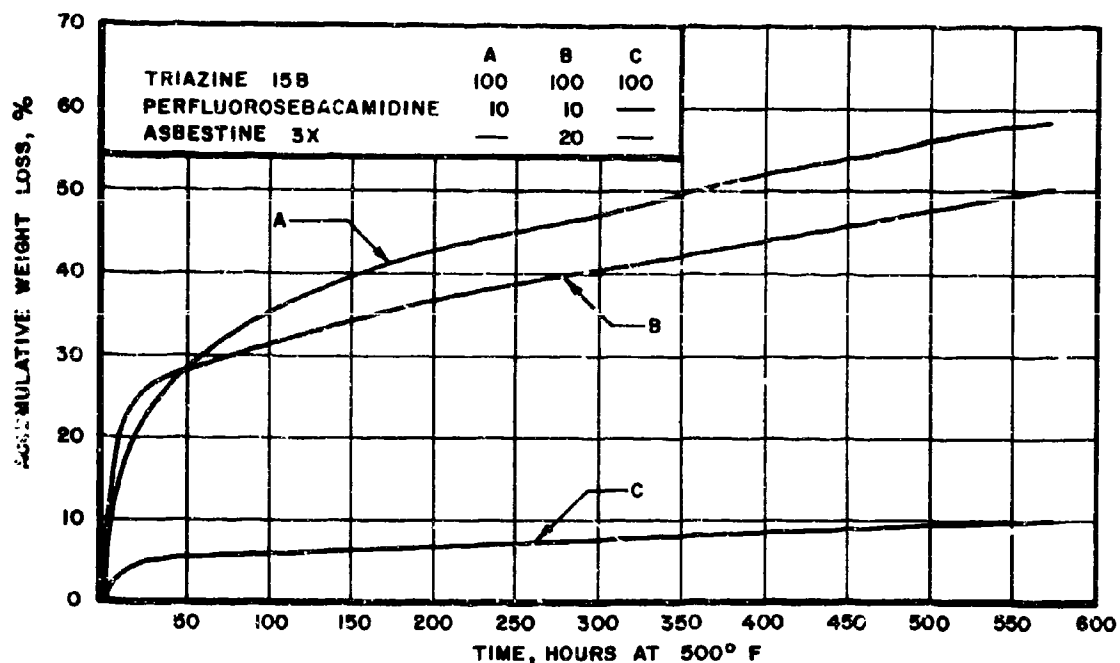


Figure 6. Effect of Asbestine 3X on the Thermal Stability of Vulcanizates Based on Poly [perfluorooctamethylene (perfluoropropyl) Triazine] Gums Containing n-Perfluoropropylene Cyanide Pendant Groups

SECTION VII

SUMMARY AND CONCLUSIONS

This internal research program was an endeavor to obtain suitable modifiers for cross-linking and reinforcing the triazine elastomers. Several samples of three different species of the triazine polymer were involved in this exploratory compounding research program.

The selected candidate reinforcing materials were screened using samples of poly[perfluoropropylene (perfluoropropyl) triazine] gum. All of the materials evaluated (carbon blacks, several microfibrinous products, metal oxide powders, mineral fillers and a perfluorinated resinous aromatic polymer bolstered the strength of the samples of poly[perfluoropropylene (perfluoropropyl) triazine] gum used in the screening experiments. The most favorable results were obtained with the asbestos fibrous fillers. Increases in strength were obtained using as much as 20 phr of a micro-fibrous asbestos filler (Asbestine 3X) at no loss in thermal stability and nominal reductions in elongation. In contrast to these results, the gains in strength realized with 15 phr of the other candidate reinforcing agents (in the case of Cab-O-Sil only 10 phr) were accompanied by significant reductions in elongation and/or increased rates of thermal decomposition.

An approach involving the use of a poly[perfluoropropylene (perfluoropropyl) triazine] resin in conjunction with asbestos filler lead to thermally cured elastomeric poly[perfluoropropylene (perfluoropropyl) triazine] products possessing good strength (565 to 900 psi). Unfortunately the vulcanizates obtained using this combination of additives proved to be extremely unstable to heat.

Experimental lots of poly[perfluorooctamethylene (perfluoropropyl) triazine] gum and n-perfluoropropylene cyanide modified poly[polyfluorooctamethylene (perfluoropropyl) triazine] gum were used for investigating the compounds selected for evaluation as curing agents. There were considerable differences in the reactivities of different lots of each of these species of the triazine polymer. While tetraphenyl tin, tetraphenyl lead and perfluoroglutarimidine proved to effective curing agents for one lot of the poly[perfluorooctamethylene (perfluoropropyl) triazine] gum, other lots of this gum could only be cured to an adequate degree using perfluoroglutarimidine. Similarly, with one lot of the poly[perfluorooctamethylene (perfluoropropyl) triazine] gum containing theoretically 20 mole percent n-perfluoropropylene cyanide pendant groups good states of cure were obtained using tetraphenyl silicon, tetraphenyl tin, tributylantimony oxide, perfluoroglutarimidine and perfluorosebacamidine whereas another sample of the modified gum could only be satisfactorily cured using the latter compound. All of these vulcanizates had low tensile strengths (245 to 325 psi) and proved to be inadequately stable in the 580° to 630°F temperature region.

Additional vulcanizates based on several of the above systems were prepared to obtain 500°F aging data as well as to determine further the merits of Asbestine 3X as a reinforcing agent. The asbestos filler improved the tensile strength of the vulcanizates but contrary to the results of initial screening experiments most generally hastened thermal decomposition. The results of 500°F aging showed the asbestos reinforced perfluoroglutarimidine and tetraphenyl tin vulcanizates based on the unmodified triazine gums to be more thermally stable than the perfluorosebacamidine cured asbestos extended n-perfluoropropylene cyanide modified poly[perfluorooctamethylene (perfluoropropyl) triazine] gums. The perfluoroglutarimidine and tetraphenyl tin asbestos reinforced poly[perfluorooctamethylene (perfluoropropyl) triazine] gums lost between 8.5 to 11.5 percent weight during the first 24 hours at 500°F. Although the rates of weight lost rapidly diminished on prolonged exposure these vulcanizates lost from 21 to 26 percent of their weight within 500 hours at 500°F and were continuing to lose weight beyond the 500-hour period at rates ranging from 0.02 to 0.03%/hour.

The mechanism whereby cured triazine products have been obtained using certain organometallic compounds and ammoniated perfluorinated dinitriles is not thoroughly understood. Although the results of experiments by Hooker Chemical with model compounds have shown certain organometallic compounds to be effective catalysts for trimerizing nitrile bearing compounds, the crosslinking reaction involving polymer appears to be more complex than the conversion of nitrile to triazine crosslinks. This conclusion is supported by the fact that an all perfluoropropyl pendant as well as perfluoropropylene cyanide modified poly[perfluorooctamethylene (perfluoropropyl) triazine] gum have been vulcanized using organometallic compounds. The triazine elastomer is a very difficult polymer to synthesize, and the possibility that some of the current products inadvertently contain in-chain reactive sites which result from incomplete reaction during the ring closure step may account for the decided differences in the reactivities of different lots of the same species of the triazine polymer towards the organometallic type curing agents. On the other hand, there is strong evidence that cured products are obtained (using the non-metallic compounds) through disruption of the basic polymer structure. In working with model compounds, Dr. H. C. Brown (Reference 3) found that nucleophiles such as NH_3 , which is liberated by the ammoniated perfluorodinitrile curing agents during the curing process, do indeed attack the triazine structure splitting out volatile chain fragments. The results of this internal research more or less corroborate Brown's work and indicate that the ammonia liberated from the non-metallic curing agents is retained and causes continual rearrangement of the cured polymer network, and in the process, polymer degradation.

The results of this work in general suggest that polymer with other functional groups may offer a better chance of success in attaining crosslinked products with the required thermal resistance. However, because of the questionable structural features of the lots of products involved in the current work there is some uncertainty regarding the adequacy of the current types of triazine polymer. In view of the foregoing uncertainty and since it is possible to prepare linear polymer by limiting the molecular weight, further exploratory work with the current species of the triazine polymer appears to be warranted, and is required to establish the future course to be pursued in the synthesis area.

SECTION VIII

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13. ABSTRACT This exploratory compounding development program was conducted for the purpose of obtaining suitable modifiers for the crosslinking and reinforcing of triazine elastomers. The reinforcing effects of a variety of finely divided materials are compared. Data are presented showing the effect of concentration of the asbestos type filler (which yielded the most promising results) on the physical properties and thermal stabilities of a poly(perfluoropropylene (perfluoropropyl) triazine) gum and a blend comprised of equal parts of the gum and a poly(perfluoropropylene (perfluoropropyl) triazine) resin. Several organometallic and organic compounds were found to be effective crosslinking agents for poly(perfluorooctamethylene (perfluoropropyl) triazine) and n-perfluoropropylene cyanide modified poly(perfluorooctamethylene (perfluoropropyl) triazine) elastomers. The physical properties and thermal resistance of chemically vulcanized gums and asbestos reinforced vulcanizates based on the n-perfluoropropylene cyanide modified and unmodified poly(perfluorooctamethylene (perfluoropropyl) triazine) gums are discussed in detail. This abstract may be further distributed by any holder <u>only</u> with specific prior approval of the Elastomers and Coatings Branch, (MANE), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, 45433.		

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